Enhanced Chemical CRUD Decontamination Combined with Electrokinetic Process – 15242

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ABSTRACT

This study has tested about the deposition and dissolution of Chalk River Unidentified Deposit (CRUD), and investigated the remediation of CRUD. CRUD is an accumulated corrosion product on external fuel rod cladding surfaces and composed of either dissolved ions or solid particles such as Ni and Co. As nuclear power plants are getting older, decontaminating process has been concerned due to increased contamination. Corrosion product can be activated through nuclear reaction to form radionuclide such as Co-60. Because the CRUD is formed at cladding surface and radionuclides can be contained in CRUD, it can affect to human health and environment. Therefore CRUD needs to be removed safely during NPP's decontaminating process by efficient. In order to decontaminate the CRUD, first thing it has to be dissolved and removed. Deposition behavior of corrosion products has been well studied, but the study about behavior of CRUD dissolution is required in various environments. In this study, the CRUD synthesis, the dissolution method of CRUD, and the CRUD decontamination method was investigated. There are three major approaches the remediation of CRUD. First one is well synthesized the CRUD, second one is finding the optimum condition for CRUD dissolution, and last one is applying the Electro-Kinetic (EK) process to CRUD remediation. Synthesis of simulated CRUD for the decontamination experiments was successful. The combination of EK process with chemical decontamination of CRUD proved to be a more economical method for removing CRUD; it can be directly applied to the NPP decommissioning and decontamination process, and it can decrease the volume of secondary radioactive waste as well.

INTRODUCTION

The process of decontaminating metals or parts of old nuclear power plant (NPP) has received greater attention lately. Decommissioning an old NPP produces intermediate and low-level radioactive wastes that need to be remediated. Because the costs of decontaminating and decommissioning NPP and any related materials are enormous, an economical remediation method is needed for radioactive waste decontamination. [1] During NPP operation, inconel and stainless steel surfaces are slowly corroded by pressurized water that circulates at high-temperature (~300℃). The corrosion product, which is called CRUD, originally deposits on the cladding, or outer coating of fuel rods. [2] CRUD has an adverse impact on fuel performance, because it also contains radioactive element such as ^{60}Co on its surface. A chemical decontamination process for CRUD formed on the metal surfaces using oxidizer and detergent agents can reduce the amount of radioactive waste and the radiation dose rate.

In order to enhance the rate of CRUD decontamination, it is important to know the chemical composition and crystalline structure of CRUD, and to develop a method to extract and remove it. The chemical composition of CRUD depends on the types of refueling cycles and the constituents of the basic material; the most representative CRUD is nickel ferrite ($NiFe_2O_4$). Co can substitute for Ni and form $CoFe_2O_4$ as CRUD. [3] In this study, $CoFe_2O_4$ was synthesized and used for CRUD decontamination testing, because Co is a radionuclide, which can affect human health. [4] The simulated CRUD ($CoFe_2O_4$) was formed as powder, and coatinged on metal specimen [SUS304 stainless steel consisting of carbon (C), silicon (Si), manganese (Mn), phosphorus (P), sulphur (S), nickel (Ni), and chromium (Cr)].

The EK remediation technology has been successfully demonstrated for the remediation of heavy metal contaminants from contaminated soils through laboratory scale and field application studies. [5-7] The combination of EK with chemical decontamination of CRUD was expected to increase the amount of contaminant removed from metal specimens. The dissolved ions migrate to their respective poles (anode and cathode) in the EK reactor. These ions can then be collected by installed zeolite, decreasing the metal concentration in the decontamination agents. Therefore, the rate of CRUD dissolving from a specimen into the chemical agent increases, and the used decontamination agent can be reused after the EK is applied. The combined chemical and EK method is one of the most promising decontamination processes for decreasing the volume of secondary waste solution with high decontamination and time efficiency while removing and collecting the contaminant from media.

The objectives of this study are to develop the decontaminating process using various decontamination reagents and synthesized CRUD. Through this study, (1) chemical composition and crystallinity of simulated CRUD were investigated and evaluated for CRUD reproducibility, (2) the efficiency of CRUD decontamination by several decontaminating agents was compared under different temperature and pH conditions for CRUD removal, and (3) chemical CRUD decontamination combined with the EK process was tested and the efficiency of the combined method was evaluated.

METHODS

Synthesis of Cobalt Ferrite ($CoFe_2O_4$)

Cobalt based CRUD which representative of the CRUD in NPP was synthesized by mixing of $FeCl_3$ (0.4M, 25mL) and $CoCl_2$ (0.2M, 25mL). The pH of mixing solution was adjusted by NaOH (3M) to 11.5. A specified amount of oleic acid (the ratio of $FeCl_3$ (0.4M, 25mL) and $CoCl_2$ (0.2M, 25mL) mixing solution vs oleic acid = 0.34:0.12) was added to the mixing solution as a surfactant and coating material. The mixing solution was reacted for 1 hr at 80 ℃, and then it was cooled to room temperature. To get free particles from sodium and chlorine compounds, the solution was centrifuged twice with distilled water and then with ethanol to remove the excess surfactant. To isolate the supernatant, the contents were centrifuged for 15 minutes at 3,000 rpm. The supernatant was decanted, and then centrifuged until only thick black precipitate remained. The precipitate was then dried for 12 hrs at 100 ℃. The substance was then grinded into a fine powder. At this stage the product contains some associated water, which was then removed by heating at 600 ℃ for 10 hrs. [8] The final CRUD was dissolved by concentrated HCl and HNO_3 (3:1) acid solution, and then chemical compositions of CRUD were determined by inductively coupled plasma mass spectrometry (ICP-MS, PerkinElmer, NexION 300D). The CRUD was also analyzed by XRD (Rigaku, D/MAX-2500/PC) for mineral identification.

Synthesis of Nickel Ferrite ($NiFe_2O_4$)

Aqueous solution (nickel nitrate (0.4M, 50mL) and ferric nitrate (0.8M, 50mL)) was prepared, and they were completely mixed with polyacrylic acid. Phase separation was observed. With constant stirring, an appropriate amount of nitric acid was slowly added to this solution until a transparent green solution (pH 1~3) was obtained. The resulting solution was evaporated at about 50℃ until a transparent sol was formed. Then, the transparent sol was heated at 50℃ for 10 hrs in order to remove water. The sol turned into a viscous brown gel.

Synthesis of CRUD on Metallic Coupon

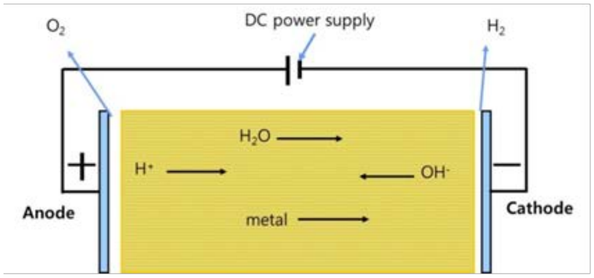
The surface of metal specimen [SUS304 stainless steel consisting of carbon (C), silicon (Si), manganese (Mn), phosphorus (P), sulphur (S), nickel (Ni), and chromium (Cr)] was abraded with silicon carbide paper (#1200). After polishing, metallic coupons were washed by acetone with ultrasonic cleaner (5 min). 0.25mL of nitrate solution (150 mg/mL) was spread on SUS 304 metallic coupon and dried. Repeat this step 4 times. Finally 1 ml of nitrate solution was doped on metallic coupon. To make oxide layer on metallic coupon surface, it was heated at 700℃, 24hrs.

Dissolution Test

20mg of powdered Ni/Co ferrite were tested respectively with chemical reagents (Oxalic acid, Malonic acid, Citric acid, and DIW as control test) for dissolution test. The pH of acids (1.8, 2.5, 3.5, 4.5, 5.5, and 6.5) was adjusted by a micropipette and 100 mL of each acid was applied to Ni/Co ferrite powder. The suspension was magnetically stirred, and temperature (70℃) and pH were continuously monitored. Reactions were carried out in the dark (the beaker was wrapped in two sheets of aluminum foil) environment. Cobalt and nickel content were determined by ICP-MS.

Decontamination Process of CRUD

Schematic diagrams of the experimental apparatus used are shown in Fig. 1. The experimental apparatus consists of four principal parts: cell, electrode compartments, electrolyte solution reservoirs, and power supply. Each electrode compartment contained a chemical reagent for removing the CRUD. Chemical reagent was recirculated in both electrode compartments using peristaltic pumps (Masterflex, 1-100 rpm, three heads), and the experimental design included the use of a BIORAD dc power supply (Mode PowerPac 200, 5-200 V, 0.01-2 A, 200 W). Control test was conducted using DIW with glass microfiber filters (GF/C, number 4, Whatman International Ltd.). Oxalic acid, malonic acid, and citric acid were used as a chemical reagent and they were applied to EK process to decontaminate the CRUD. A number of physicochemical parameters were measured every 1h during the experiments. Concentration of Co and Ni were analyzed by ICP/MS.



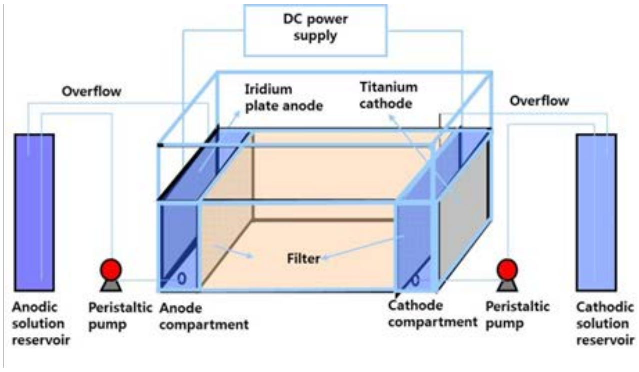


Fig. 1. Schematic diagrams of the experimental apparatus (EK process)

RESULTS

Synthesis of Cobalt Ferrite ($CoFe_2O_4$)

The X-Ray Diffraction (XRD) result of synthesized $CoFe_2O_4$ was shown in Fig.2, Scanning Electron Microscopy with X-ray microanalysis (SEM/EDS) results of synthesized $CoFe_2O_4$ was shown in Fig. 3, and the X-Ray Fluorescence (XRF) result of synthesized $CoFe_2O_4$ was shown in Table 1. All of the results show that Co based CRUD was well synthesized in our method. It is identified as Co-ferrite [$CoFe_2O_4$].

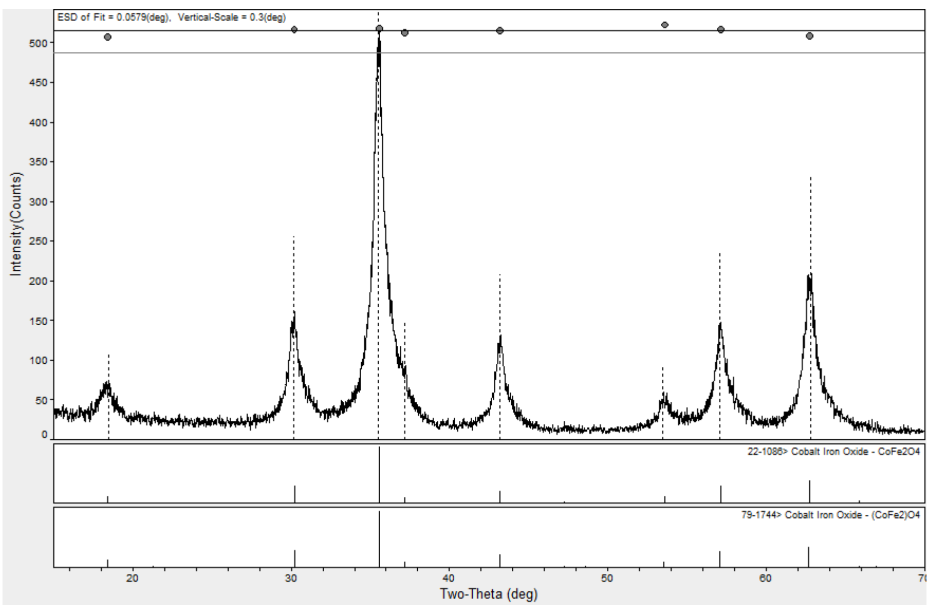


Fig. 2. XRD of $CoFe_2O_4$

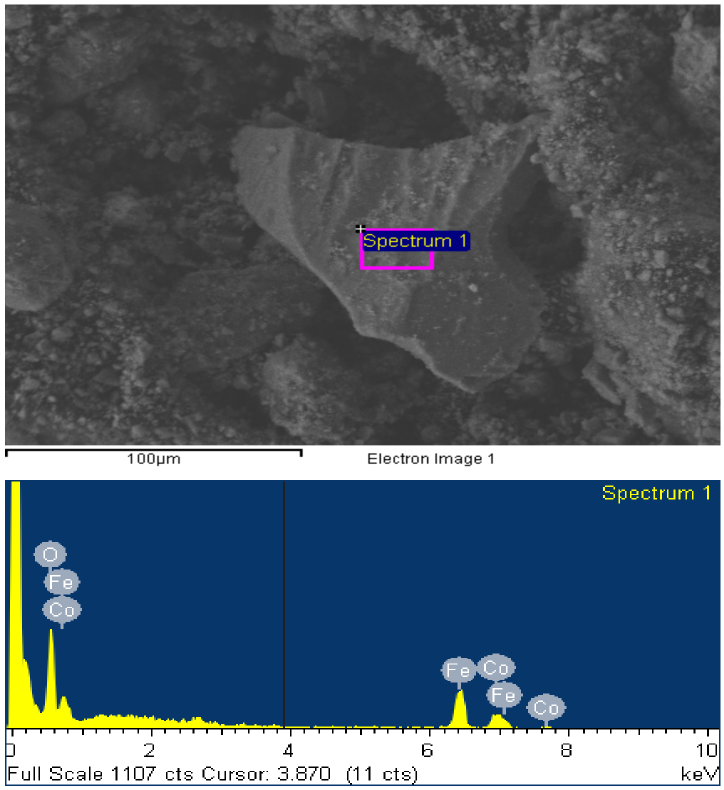


Fig. 3. SEM/EDS result of $CoFe_2O_4$

TABLE I. XRF data of $CoFe_2O_4$

Compound formula	Normalized concentration (%)
Co	31.44
Fe	65.61
Ni	0.0442

Synthesis of CRUD on Metallic Coupon

Fig. 4 shows the synthesized CRUD on metallic coupon, and SEM/EDS results of synthesized CRUD on metallic coupon was shown in Fig. 5. In Fig. 5, SEM/EDS results shows CRUD was well formed on the surface of metallic coupon

Fig. 4. Synthesis of CRUD on metallic coupon

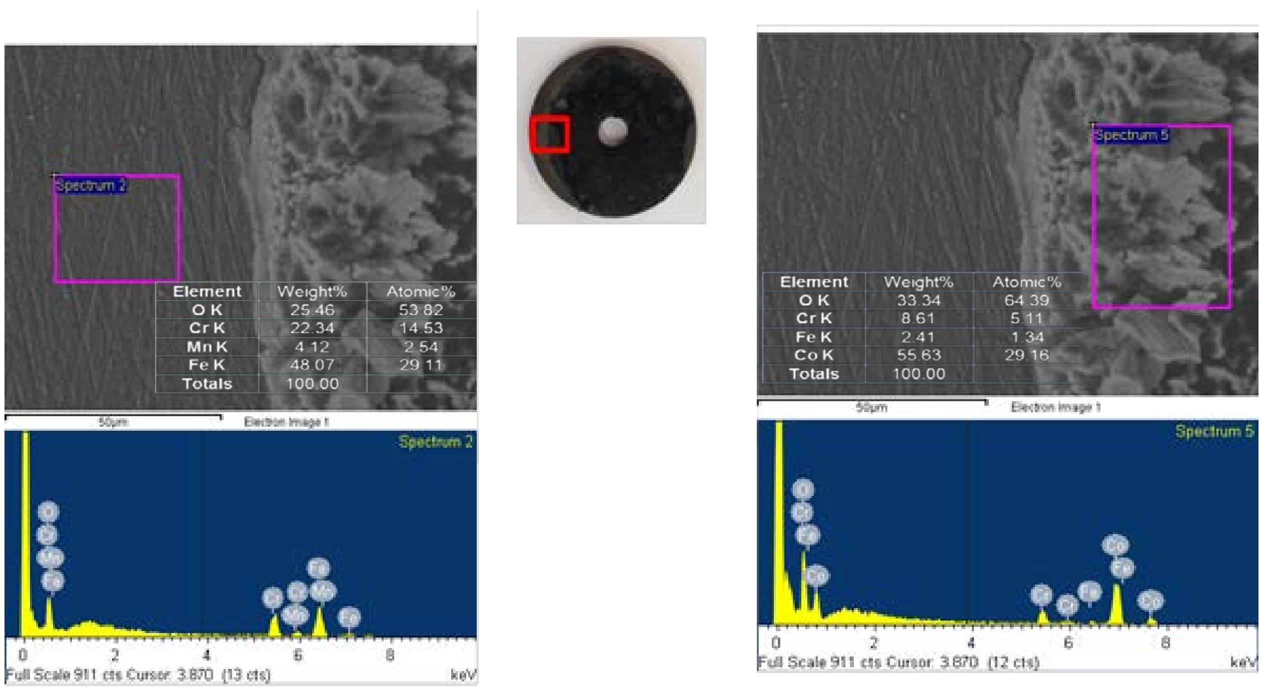


Fig. 5. SEM/EDS result of synthesis of CRUD on metallic coupon

Dissolution Test

Optimum decontamination condition for CRUD dissolution was tested with different chemical reagent and various pH. Fig. 6 shows the dissolved Co concentration in each pH with respectively chemical reagents. Small amount of Co dissolved over the pH = 4.5 in every chemical reagents. The dissolution amount of Co was high in low pH = 3.5 respectively and the oxalic acid has the best capacity as a chemical reagent to make dissolve the CRUD.

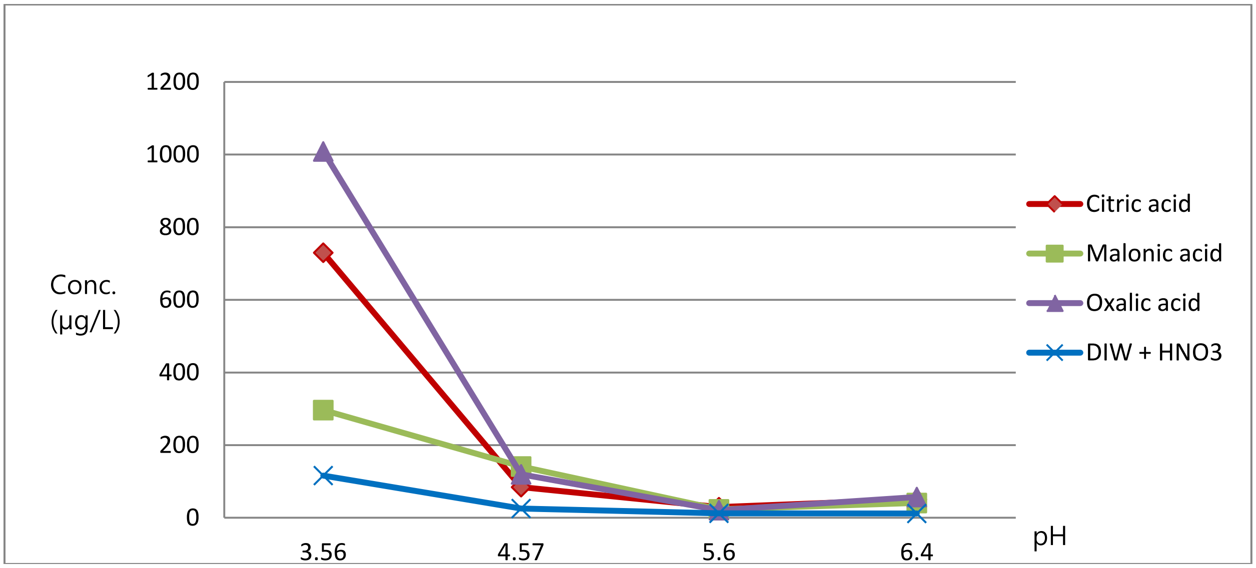


Fig. 6. The concentration of Co with different chemical reagent and pH in dissolution test

Decontamination Process of CRUD

CRUD decontamination process test is still being investigated using different decontamination reagents with different conditions. In order to test the decontamination process by EK reactor, the CRUD was put in the middle of EK reactor and chemical reagent was circulated by pump. The electric power was supplied and the dissolved cation was moved by electric current to cathode. Fig. 7 shows the Co concentration on the cathode compartment in EK reactor. Although the oxalic acid is the best chemical reagent for dissolving the Co from CRUD, the Co concentration in cathode compartment of EK reactor is very low. Because the pH is high (9-10) in cathode compartment of EK reactor during EK process running, the Co, which transported to cathode, was precipitated by Co complex with hydroxide ion. It means that dissolved Co by oxalic acid during EK process can move to cathode part in EK reactor, and then transported Co was removed in cathode part by hydroxide ion which occurred by EK process. Combined with chemical reagent and the EK process was tested for CRUD decontamination, and more effective method will be investigated and evaluated.

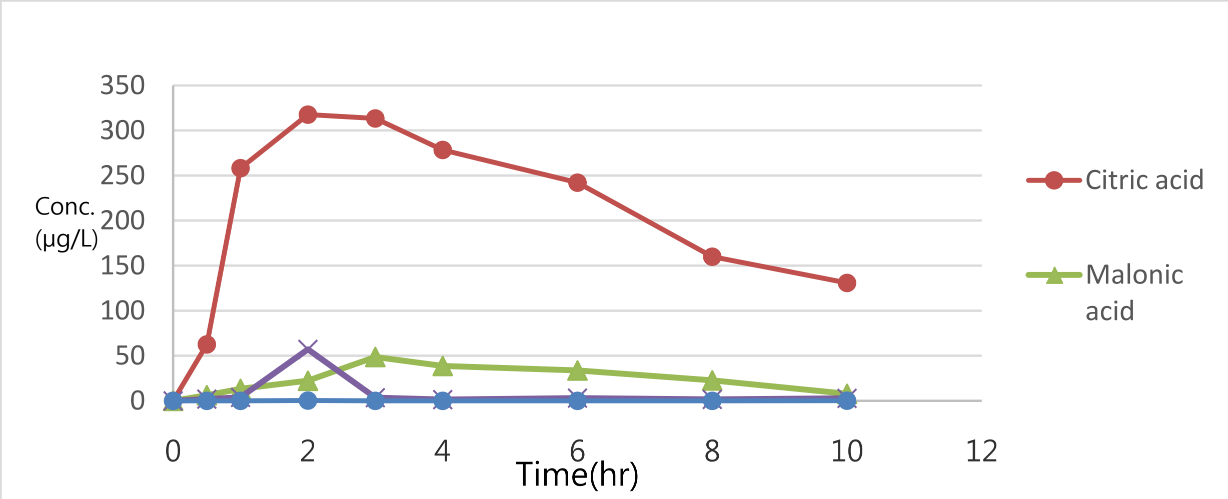


Fig. 7. The Co concentration on the cathode compartment in EK reactor

CONCLUSION

Simulated CRUD was successfully synthesized and characterized. Effective CRUD decontamination process was tested by different chemical reagent with different condition, and more optimum condition should be determined to remove CRUD. In order to both enhance the removal efficiency and minimize the volume of contaminated liquid, the EK process was introduced into the CRUD decontamination process. The EK method can apply to decontamination process, and the combined with chemical CRUD decontamination and the combined EK process with chemical reagent was tested. The more efficiency and enhanced combined method need to be investigated and evaluated.

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